

DTIC FILE COPY

2

WRDC-TR-90-4064



AD-A227 529

THE EFFECT OF JET FUEL EXPOSURE ON ADVANCED
AEROSPACE COMPOSITES II: MECHANICAL PROPERTIES

D.B. Curliss and D.M. Carlin
Structural Materials Branch
Nonmetallic Materials Division

AUGUST 1990

Final Report for Period May 1989 - December 1989

Approved for public release; distribution is unlimited



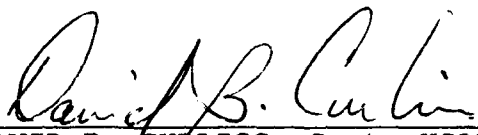
MATERIALS LABORATORY
WRIGHT RESEARCH AND DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6533


NOTICE

WHEN GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY GOVERNMENT-RELATED PROCUREMENT, THE UNITED STATES GOVERNMENT INCURS NO RESPONSIBILITY OR ANY OBLIGATION WHATSOEVER. THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATION, OR OTHER DATA, IS NOT TO BE REGARDED BY IMPLICATION, OR OTHERWISE IN ANY MANNER CONSTRUED, AS LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION; OR AS CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.


THIS REPORT IS RELEASABLE TO THE NATIONAL TECHNICAL INFORMATION SERVICE (NTIS). AT NTIS IT WILL BE AVAILABLE TO THE GENERAL PUBLIC, INCLUDING FOREIGN NATIONS.

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION


DAVID B. CURLISS, Capt, USAF
Structural Materials Branch
Nonmetallic Materials Division


CHARLES E. BROWNING, Chief
Structural Materials Branch
Nonmetallic Materials Division

FOR THE COMMANDER


MERRILL L. MINGES
Director
Nonmetallic Materials Division

IF YOUR ADDRESS HAS CHANGED, IF YOU WISH TO BE REMOVED FROM OUR MAILING LIST, OR IF THE ADDRESSEE IS NO LONGER EMPLOYED BY YOUR ORGANIZATION, PLEASE NOTIFY WRDC/MLBC, WRIGHT-PATTERSON AFB, OH 45433-6533 TO HELP MAINTAIN A CURRENT MAILING LIST.

COPIES OF THIS REPORT SHOULD NOT BE RETURNED UNLESS RETURN IS REQUIRED BY SECURITY CONSIDERATIONS, CONTRACTUAL OBLIGATIONS, OR NOTICE ON A SPECIFIC DOCUMENT.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release, distribution is unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) WRDC-TR-90-4064		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Materials Laboratory WRDC/MLBC	6b. OFFICE SYMBOL (If applicable) WRDC/MLBC	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Wright-Patterson AFB, OH 45433-6533		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 62102F	PROJECT NO. 2419
		TASK NO. 03	WORK UNIT ACCESSION NO. 45
11. TITLE (Include Security Classification) The Effect of Jet Fuel Exposure on Advanced Aerospace Composites II: Mechanical Properties			
12. PERSONAL AUTHOR(S) David B. Curliss and Diana M. Carlin			
13a. TYPE OF REPORT FINAL	13b. TIME COVERED FROM MAY 89 TO DEC 89	14. DATE OF REPORT (Year, Month, Day) August 1990	15. PAGE COUNT 23
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Advanced Composites, Fluid Exposure	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) → The sensitivity of several advanced aerospace composite materials to military jet fuel, JP-4, was investigated in this study. The following commercially available fiber/matrix prepreg materials were used in this investigation: AS-4/3501-6; IM7/8551-7A; IM7/977-2 (1377-2T); IM7/5250-4; IM8/HTA; and AS-4/PEEK(APC-2). The materials were chosen as representative state-of-the-art materials in their classes of standard epoxy, toughened epoxy, toughened BMI, and thermoplastic matrix composites respectively. The materials were processed into $[±45]_2S$, $[0]_{12}T$, and $[90]_{12}T$ laminates using the manufacturer's recommended process cycle and standard quality assurance checks were performed on the panels. Standard geometry coupons were fabricated from the panels and divided into a control set and test set. The test coupons were immersed in JP-4 in a sealed pressure vessel at 180°F. The weight gain was recorded as a function of the square root of time and the jet fuel was exchanged each time the coupon weight was recorded. In general, the thermoset matrix composites did not pick-up significant levels of fuel in any lay-up examined; while the thermoplastics did absorb JP-4. The amount of JP-4 absorbed by the thermoplastic matrix composites was dependent on the lay-up. After 1680 hours of total exposure time the mechanical properties of the coupons were evaluated. G_{12} was determined from the $[±45]_2S$ coupons and E_{flex} and $σ_{flex}$ were determined for the $[0]_{12}T$ and $[90]_{12}T$ coupons. G_{12} for the thermoplastic matrix composites was markedly lower at elevated temperatures in the fuel exposed specimens than in the control specimens, due to plasticization of the matrix. The 0° and 90° thermoset matrix composites flexure specimens exposed to JP-4 had lower strengths than did the control specimens. The lower strength is attributed to degradation of the interface between the fiber and matrix. Scanning electron microscopy was used to examine the failure surfaces. The flexure modulus in the 90° flexure specimens was not affected by exposure to JP-4 while the 0° flex modulus was lower in the fuel exposed coupons than in the control coupons.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL DAVID B. CURLISS		22b. TELEPHONE (Include Area Code) (513) 255-9069	22c. OFFICE SYMBOL WRDC/MLBC

TABLE OF CONTENTS

SECTION	PAGE
1. INTRODUCTION.....	1
2. EXPERIMENTAL PROCEDURES.....	2
2.1 Sample Preparation.....	2
2.2 Jet Fuel Exposure.....	3
2.3 Thermal Analysis.....	5
2.4 Dynamic Mechanical Analysis.....	5
2.5 Mechanical Testing.....	5
2.5.1 Four-Point Flexure Testing.....	5
2.5.2 +/- 45° Tension Testing.....	7
2.6 Scanning Electron Microscopy.....	7
2.7 Desorption Analysis.....	7
3. RESULTS AND DISCUSSION.....	7
3.1 Jet Fuel Exposure Results.....	7
3.2 Thermal Analysis Results.....	12
3.3 Dynamic Mechanical Results.....	13
3.4 Mechanical Testing Results.....	13
3.4.1 0° Four-Point Flexure Results.....	13
3.4.2 90° Four-Point Flexure Results.....	15
3.4.3 0° Four-Point Shear Results.....	15
3.4.4 +/- 45° Tension Results.....	15
3.5 Scanning Electron Microscopy Results.....	16
3.6 Desorption Results.....	16
4. CONCLUSIONS.....	18
5. REFERENCES.....	18

LIST OF FIGURES

FIGURE	PAGE
1. Pressure vessel used to expose composite coupons to JP-4.....	4
2. Vacuum desorption apparatus for composites exposed to jet fuel.....	8
3. Weight gain versus time ^{1/2} for APC-2 and IM8/HTA [+/-45°] _{2S} coupons.....	9
4. Weight gain versus time ^{1/2} for AS4/3501-6, IM7/8551-7A, IM7/977-2, IM7/5250-4 [+/-45°] _{2S} coupons.....	10
5. Weight gain versus time ^{1/2} for all thermoplastic and thermoset matrix [0°] _{12T} composite coupons.....	11
6. Scanning Electron Microscope photograph of the [90°] _{12T} flex failure surface of IM7/8551-7A control specimen.....	17
7. Scanning Electron Microscope photograph of the [90°] _{12T} flex failure surface of IM7/8551-7A specimen exposed to JP-4.....	17

LIST OF TABLES

TABLE	PAGE
1. Materials and Process Conditions Used.....	3
2. Mechanical Test Matrix for JP-4 Exposure Study.....	6
3. Dynamic Mechanical Analysis Results.....	13
4. Mechanical Test Results.....	14
5. GC-MS Results (Octane is used as reference).....	18



Accession No.	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input checked="" type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of the University of Dayton Research Institute personnel for performing some of the material characterization and mechanical testing reported here. We would also like to thank Michael S. Arnett of Wright State University for his many hours in the laboratory preparing the specimens for testing and fluid absorption.

1. INTRODUCTION

The issue of the interaction between organic matrix composite materials and fluids which they may be exposed to during their lifetime has been controversial. It is well understood that advanced composites utilizing thermosetting resins absorb moisture when exposed to high humidity environments. The absorption of moisture causes plasticization of the resin with concurrent swelling and lowering of the resin's glass transition temperature (T_g). This results in a reduced service temperature of the composite. This phenomena has been studied and well characterized (1,2). Composite materials are typically tested after exposure to temperature and humidity to determine the reduction in mechanical properties.

The effects of other aircraft fluids which are in contact with these materials over their lifetime has not been as well characterized. There are no current industry standards to assess possible effects. A typical exposure test may involve submersion of the materials in the fluid at room temperature for seven days. The material is then mechanically tested at room temperature. Typically no reduction in properties occurs from this type of exposure. Therefore, it is concluded that the fluids tested have no significant effect on the mechanical properties and that a "hot/wet" exposure represents the worst case environmental conditions.

Recent investigations of thermoplastic matrix composites have determined that these materials absorb some aircraft fluids (3,4). An attempt was made to correlate this data with other fluid studies. However, because there are no current industry standards for testing fluid exposure, it was impossible to compare or correlate any existing data.

An Air Force sponsored study was conducted (5) in an attempt to assess current industry practice for testing composites in fluids. The procedures employed by companies surveyed were so varied that it was extremely difficult to correlate data from one participant to another. These variations ranged from the number of plies and orientation to the choice of fluid, exposure time, and exposure conditions.

Aircraft composites may be exposed to relatively aggressive fluids, such as jet fuel at elevated temperatures, on a daily basis for as long as 20 or 30 years. Because of this it is important to gain a fundamental understanding of the effects of aircraft fluids on composite materials. Several issues have been raised relative to the sensitivity of advanced

composites to aircraft fluids. These include: a) realistic temperatures and time, b) the definition of typical in-service mechanical state during exposure, c) the development or selection of a mechanical test to measure the effects of fluid exposure on composites, and d) understanding the mechanisms of interaction between the fluid and the composite.

In this study we have adopted the approach of trying to gain a better understanding of the fundamental mechanisms of interaction of the aircraft fluid with the composite. Our view is that if the fundamental mechanisms of interaction are understood then this information can be used to understand the effect of fluid interaction on the macroscopic properties of more complex composite materials. This approach includes exposure of the composite at an elevated temperature until saturation (or apparent saturation) is achieved, weight gain versus time and coupon configuration, determination of diffusion mechanisms, effects of weight gain on physical and mechanical properties, and absorption/desorption studies.

There are several aircraft fluids of concern. Hydraulic fluid, paint strippers, cleaners, and jet fuel are among those of most concern. In this study we have chosen to evaluate only the effect of jet fuel since very little is known about this and also because it is very difficult to protect the composite from this fluid.

2. EXPERIMENTAL PROCEDURES

2.1 Sample Preparation The materials used in this study, the supplier of the material, and the cure or consolidation cycle used are given in table 1. The cure or consolidation cycles are those recommended by the supplier and in all cases were found to give quality laminates. The thermoset materials were all autoclave cured using a standard net resin bagging technique; the thermoplastic materials were all press consolidated. After processing, the panels were C-scanned to verify that they were free of porosity. Photomicrograph specimens were also made from several different sections in the laminates to verify uniform fiber distribution. Acid digestion of specimens taken from various sections of the laminates was used to obtain the fiber volume of each laminate. Differential Scanning Calorimetry, Thermogravimetric Analysis, and Thermomechanical Analysis were also used to verify that the laminates were of expected quality. Test specimens were cut from laminates using a water-cooled diamond impregnated saw and the edges were finished using a fine grit paper. All specimens were then dried in a vacuum oven and weighed and measured. The control specimens were stored in a desiccator until testing, and the exposure specimens were immediately placed in the exposure vessels.

Table 1. Materials and Process Conditions Used.

<u>Material</u>	<u>Supplier</u>	<u>Cure Cycle</u>
AS-4/3501-6	Hercules	Heat to 116°C, 60 min. @ 586 KPa. Heat to 177°C, 6 hrs. @ 655 KPa.
IM7/8551-7A	Hercules	Heat to 180°C, 250 min. @ 620 KPa.
IM7/977-2(1377-2T)	ICI/Fiberite	Heat to 99°C, 60 min. @ 690 KPa. Heat to 177°C, 3 hrs. @ 690 KPa.
IM7/5250-4	BASF/Narmco	Heat to 149°C, 45 min. @ 586 KPa. Heat to 191°C, 6 hrs. @ 586 KPa. Post-cure @ 227°C for 6 hrs.
AS-4/PEEK(APC-2)	ICI/Fiberite	Heat to 382°C, 30 min. @ 1379 KPa.
IM8/APC(HTA)	ICI/Fiberite	Heat to 357°C, 30 min. @ 1379 KPa.

2.2 Jet Fuel Exposure Military jet fuel, type JP-4, was used in this study as the exposure fluid. JP-4 is an extensively used jet fuel and is a more aggressive solvent than another widely used jet fuel, JP-8. JP-8 has lower levels of low molecular weight aromatic hydrocarbons and is also less volatile than JP-4. Therefore, JP-4 was chosen as a "worst case" fluid.

Composites may be exposed to jet fuel at temperatures greater than ambient because of several factors such as aerodynamic heating of the structures and radiant heating. Fuel may even be used as a cooling medium in aircraft systems and is heated in the process. We chose 82°C as a representative temperature for exposure of the composites to fuel. Specially made vessels were used to contain the jet fuel and coupons at temperature. Figure 1 is a schematic of the vessel. The vessels were constructed of stainless steel aircraft hydraulic tubing. The vessels were completely filled with JP-4 and the composite coupons. This was done to prevent differences in liquid and vapor phase compositions of the JP-4. The low molecular weight aromatic components of the jet fuel are likely to absorb into the composites to the greatest extent; therefore an effort was made to ensure that these components were of the highest possible concentration in the liquid phase. The specimens were sealed in the vessel and then the vessels were placed into an inert atmosphere convection oven at temperature. Periodically the vessels were cooled down and the specimens were wiped off and weighed. At each weighing the fuel was exchanged with fresh fuel from the same batch. The exchange was done in an attempt to maintain the same composition in the exposure vessel. The coupons were exposed to jet fuel for a total of 1680 hrs.

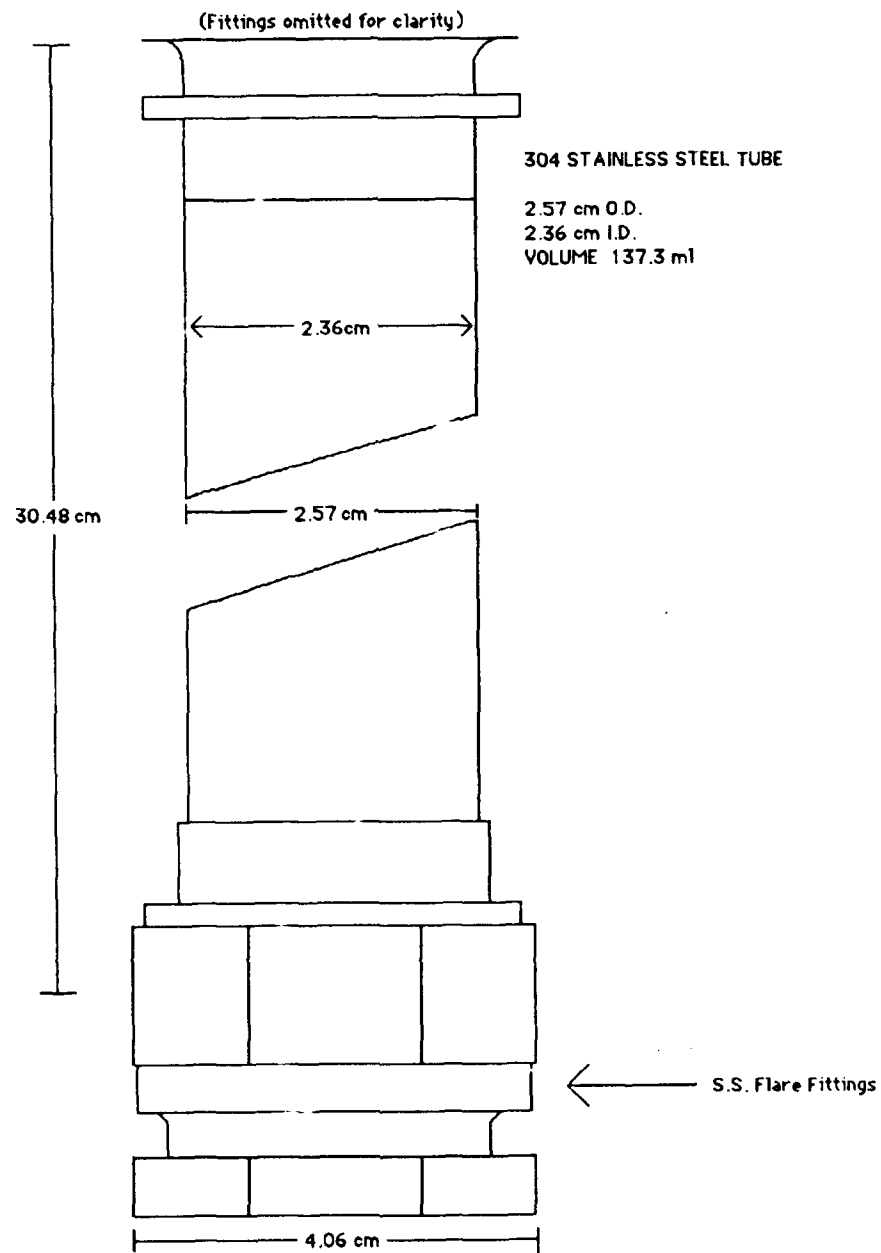


Figure 1. Pressure vessel used to expose composite coupons to JP-4.

2.3 Thermal Analysis Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Thermomechanical Analysis (TMA) were performed on each laminate produced and on specimens after exposure to JP-4. DSC was performed with a DuPont Model 910 DSC, TGA was performed with a DuPont Model 951 TGA, and TMA was performed with a DuPont Model 943 TMA. The DuPont equipment was controlled with an OmniTherm Advantage II IBM PS/2-60 data station. Sample size ranged from 5 mg to 15 mg for the DSC and TGA while the TMA used 6 mm X 6 mm X laminate thickness for samples. TMA and TGA were performed under an inert atmosphere. All tests were performed at a standard heating rate of 10°C/min. In addition to standard quality assurance, TGA isothermal aging was performed on laminates after exposure to JP-4 to determine if weight change during mechanical testing at elevated temperatures would be a problem. The specimens were aged at their maximum test temperature up to 45 min. and showed no measurable weight loss due to fuel desorption.

2.4 Dynamic Mechanical Analysis Dynamic Mechanical Analysis (DMA) was performed on both the control and fuel exposed specimens. The $[0^\circ]_{12T}$ coupons were used in a forced torsion geometry on a Rheometrics RDS-II dynamic mechanical spectrometer. The shear storage and loss moduli were determined as a function of temperature at 1Hz ($G'(T)_{\omega=1\text{Hz}}$ and $G''(T)_{\omega=1\text{Hz}}$). The heating rate used was 10°C/min. These data were used to determine the T_g of the coupons, for a quality control check and also to determine if there is a detectable T_g depression due to the fuel absorption.

2.5 Mechanical Testing The mechanical test matrix used to evaluate the effect of the jet fuel exposure is given in Table 2. The tests (with the exception of 90° flex and 0° four point shear) were conducted at room temperature, 82°C, and an elevated temperature indicated in Table 2. These temperatures were chosen low enough to be in the elevated temperature dry service range of the composites, but high enough to see the effect of the JP-4 on the properties. The span-to-depth ratio was 32:1 for the 0° and 90° four point flex tests and 16:1 for the 0° four-point shear.

2.5.1 Four Point Flexure Testing The four-point flex testing was performed in accordance with ASTM standard D790-81 on an Instron test frame. The crosshead speed in all flex and the 0° four-point shear was 0.127cm/min. Crosshead displacement was used to calculate mechanical properties for the 0° flex and 0° shear, while the 90° flex specimens were strain gauged on their tensile surface.

Table 2. Mechanical Test Matrix for JP-4 Exposure Study

MATERIAL	CONDITION	0° 4-PT Flex*		90° 4-PT Flex* 0° 4-PT Shear*		+/-45° Tension**	
		RT	82 °C	ET1***	RT	RT	82 °C ET1***
AS-4 / 3501-6	CONTROL	3	3	3	3	3	3
	JP-4	3	3	3	3	3	3
IM-7 / 5250-4	CONTROL	3	3	3	3	3	3
	JP-4	3	3	3	3	3	3
IM-7 / 8551-7A	CONTROL	3	3	3	3	3	3
	JP-4	3	3	3	3	3	3
IM-7 / 977-2	CONTROL	3	3	3	3	3	3
	JP-4	3	3	3	3	3	3
AS-4 / PEEK (APC-2)	CONTROL	3	3	3	3	5	5
	JP-4	3	3	3	3	5	5
IM-8 / APC (HTA)	CONTROL	3	3	3	3	3	3
	JP-4	3	3	3	3	3	3

*** ET1
 149 °C
 121 °C
 177 °C
 149 °C
 121 °C
 177 °C

* ASTM # D790-81
 length = 6.35 cm
 width = 1.14 cm
 thickness = 0.16 cm

** ASTM# D3518-76(82)
 length = 13.9 cm
 width = 1.91 cm
 thickness = 0.10 cm

2.5.2 +/- 45° Tension Testing The +/- 45° tension testing was performed in accordance with ASTM standard D3518-76(82) on an MTS test frame. The samples were all strain gauged and the loading rate was 44.5N/sec. The specimens were only tested to approximately 0.3% axial strain so end-tabbing was not necessary.

2.6 Scanning Electron Microscopy The 90° flex failure surfaces and the "3-direction" surface of the 90° flex control and fuel exposed coupons were examined using a JEOL 840 scanning electron microscope. The samples were coated with Palladium-Gold and examined using 10kV. The "3-direction" surface was examined for crazing due to fuel exposure, and the failure surfaces were examined for fiber/matrix adhesion and any other characteristics of the 90° flex failure.

2.7 Desorption Analysis A specially designed apparatus was used to extract and trap the components of jet fuel that were absorbed into the composite specimens. This apparatus is shown schematically in Figure 2. The fuel exposed coupons are loaded into the sample chamber and the entire apparatus is repeatedly purged with nitrogen to remove all air then evacuated under continuous vacuum. The chamber is heated to approximately 316°C and held for 1 hr. Any volatiles from the laminates are collected in the cold trap. The desorption process is quantitative, as the weight of the laminates after desorption is identical to their weight before exposure to JP-4. The condensate is diluted with spec grade n-pentane and collected. The samples are then analyzed using GC-MS. This technique allows for separation of the components in the mixture (GC) and their identification (MS). This technique can also be used to qualitatively determine the relative amount of each component in the mixture.

3. RESULTS AND DISCUSSION

3.1 Jet Fuel Exposure Results The weight gain plotted versus the square root of time is shown for the [+/-45°]_{2S} coupons in Figures 3 and 4 and for the [0°]_{12T} in Figure 5. The weight gain trends of the [90°]_{12T} coupons were identical to the [0°]_{12T} specimens so that data is not presented.

The [+/-45°]_{2S} thermoplastic laminates, APC-2 and the IM8/HTA, both picked up approximately 0.85weight percent (wt%) jet fuel and reached an apparent saturation value. However, in the 0° and 90° unidirectional coupons the APC-2 did not pick up a significant amount of jet fuel and the IM8/HTA absorbed only approximately 0.35wt%. This

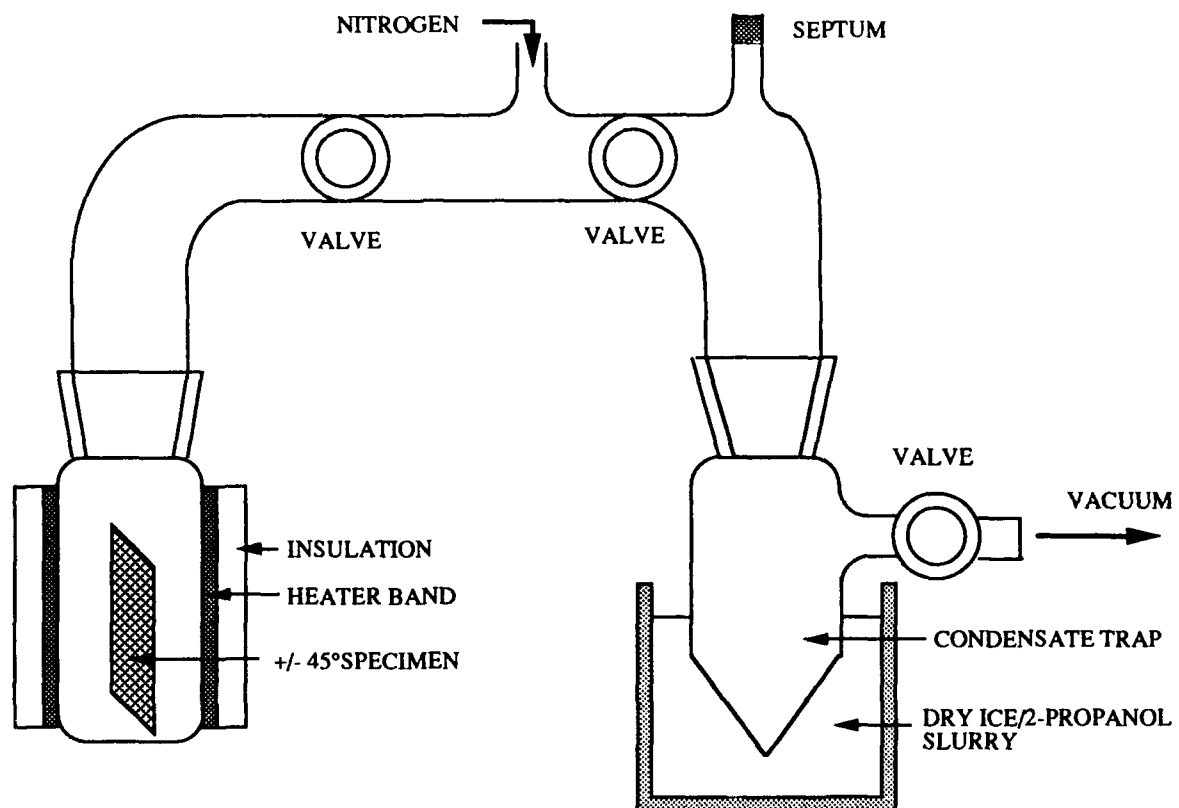


Figure 2. Vacuum desorption apparatus for composites exposed to jet fuel.

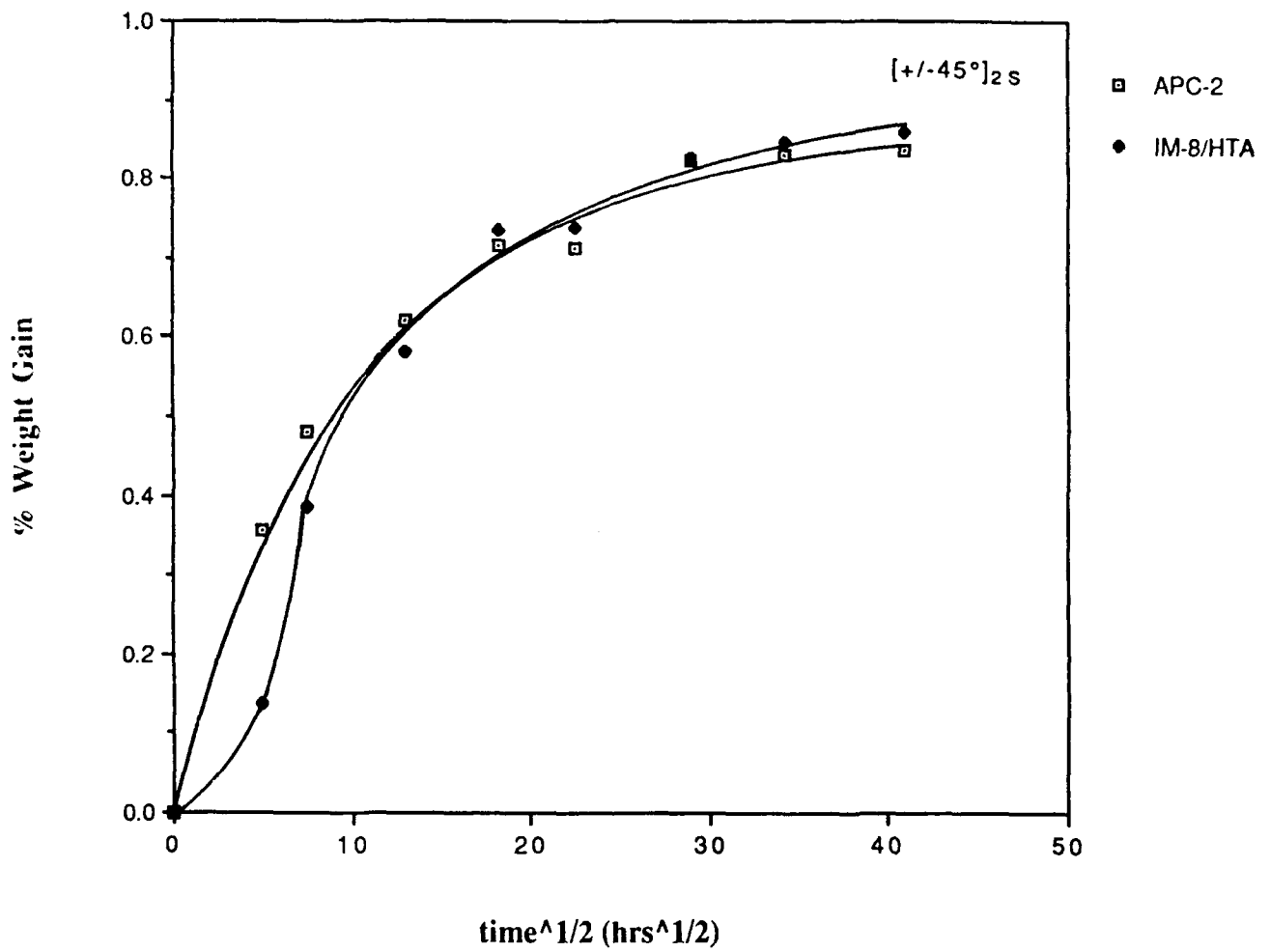


Figure 3. Weight gain versus time^{1/2} for APC-2 and IM-8/HTA [+/-45°]_{2s} coupons.

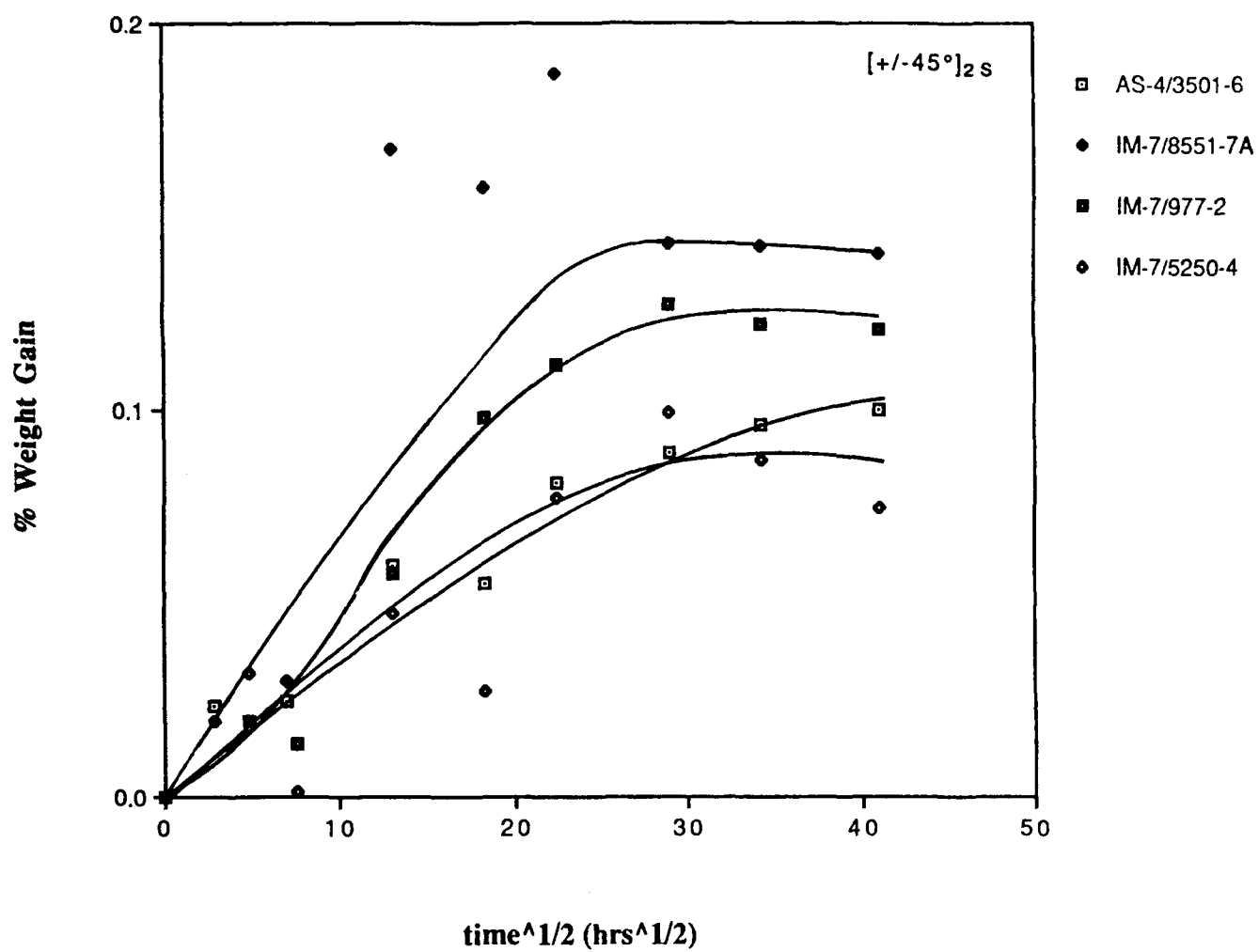


Figure 4. Weight gain versus time^{1/2} for AS-4/3501-6, IM-7/8551-7A, IM-7/977-2, IM-7/5250-4 [+/-45°]_{2s} coupons.

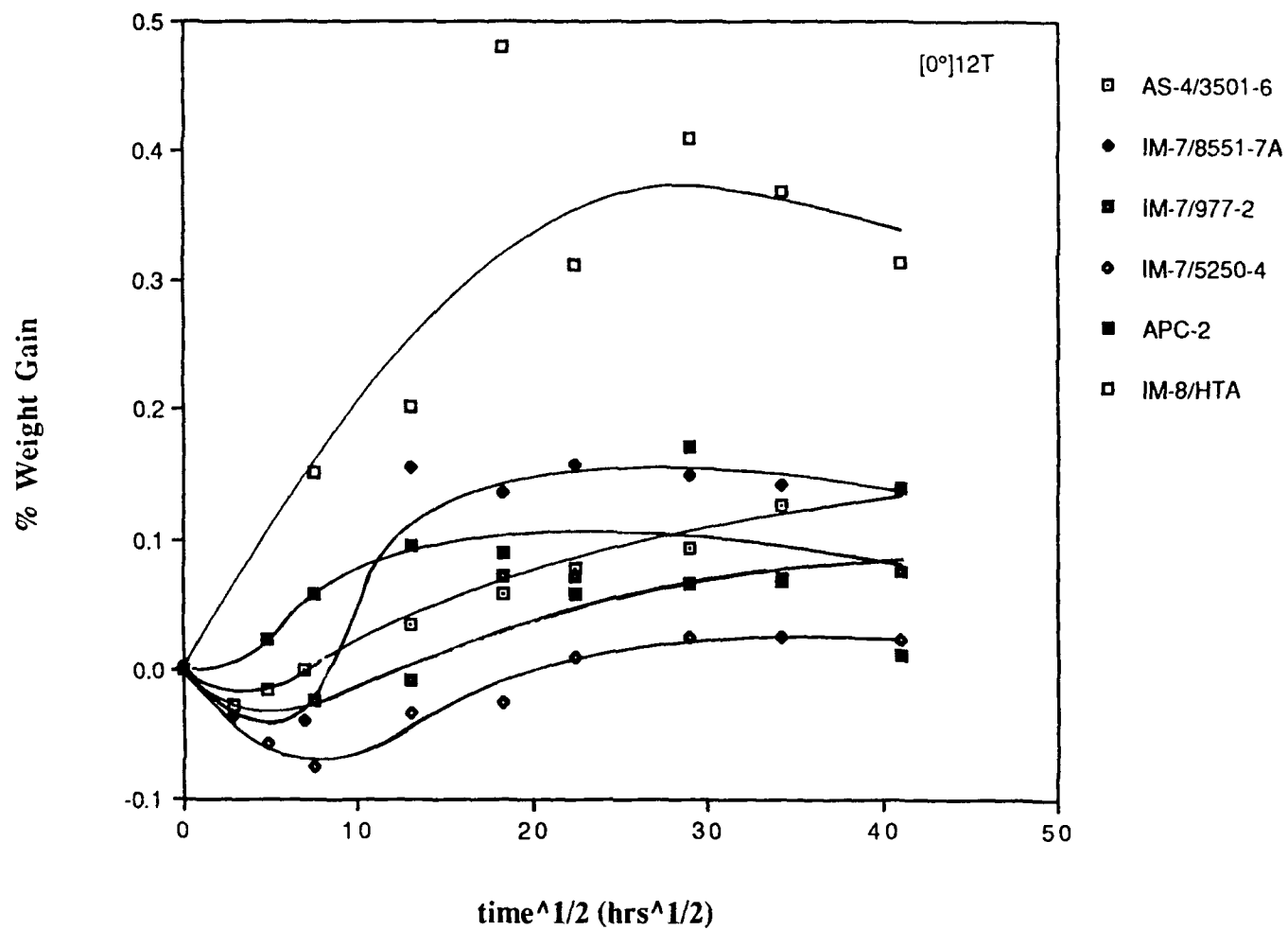


Figure 5. Weight gain versus $\text{time}^{1/2}$ for all thermoplastic and thermoset matrix $[0^\circ]_{12T}$ composites.

difference may be attributed to several factors such as residual stress, crystallinity and crystal morphology (in APC-2), fiber wicking, or microcracks. If fiber wicking were responsible for the observed difference there should be a difference between the 0° and 90° unidirectional coupons. However, these configurations have virtually identical weight gain characteristics. Thus, fiber wicking has been ruled out in this case. Photomicrographs of the $\pm 45^\circ$, 0° , and 90° coupons show no microcracking so this has been ruled out as a cause of the difference. The crystal morphology of the APC-2 may be different in the angle ply laminates and the unidirectional laminates, but this was not investigated in this study. WAXS will be used in further investigations to determine the effect of crystal morphology on jet fuel absorption. The state of stress in a polymer has been directly related to the diffusion of solvents (6) in polymers and this is the most likely reason for the difference in absorption characteristics between the different laminate configurations.

The thermoset matrix laminates, with the exception of IM7/8551-7A, absorbed less than 0.1wt% in all laminate configurations. There was also large scatter in the measurements because of the low level of fuel absorbed and the small number of coupons exposed. The IM7/8551-7A system had a very pronounced weight gain between 48 hrs and 168 hrs, after which the weight gain remained constant within the scatter. The 8551-7A is a very complex heterogeneous resin system. The unusual absorption characteristics are attributed to the complex phase structure of the resin.

No attempt has been made to model the diffusion behavior of the composites from this data. Much more testing will be required to make any conclusions about the nature of the diffusion process.

3.2 Thermal Analysis Results The thermal analysis performed on the control specimens was used primarily for quality assurance, verifying that the T_g , crystallization temperature (T_c), and endotherm peaks were all characteristic of the materials evaluated. Thermal analysis on the fuel exposed specimens was performed to detect changes in T_g and phase transitions. The thermoset matrix composites did not absorb any appreciable jet fuel, and there are no significant changes in their DSC, TMA, or TGA scans. The APC-2 DSC scan did have a larger heat of crystallization for the $\pm 45^\circ$ laminate configuration exposed to jet fuel than for the $\pm 45^\circ$ control coupon. TGA-MS results have indicated that there is a large volatile evolution that occurs with the crystallization transition. This could contribute to the larger heat of crystallization. The TMA scan of the APC-2 $\pm 45^\circ$ exposed to JP-4 indicated a T_g of 106°C . This is an approximately 40°C decrease in the T_g for the fuel soaked

coupons. The TMA of the IM8/HTA specimen did not yield a distinct glass transition. The thermal analysis data are presented in their entirety in a separate report (7).

3.3 Dynamic Mechanical Results The results of the DMA are summarized in Table 3. There was very little effect of the jet fuel on AS-4/3501-6 and IM7/977-2, but all of the other materials experienced drop in their T_g, as measured by the storage and loss modulus respectively. The T_g from the storage modulus transition for APC-2 is 137°C as opposed to 106°C from the TMA measurement. This is due to the large difference in solvent content between the $[+/-45^\circ]_{2S}$ (0.84wt% JP-4) coupon used for the TMA and the $[0^\circ]_{12T}$ (0.005wt% JP-4) coupon used for the DMA measurements.

Table 3. Dynamic Mechanical Analysis Results.

Material	Control, G'	JP-4, G'	Control, G''	JP-4, G''
AS-4/3501-6	181	182	205	200
IM7/8551-7A	195	181	219	206
IM7/5250-4	243 (272)	258	266 (313)	276
IM7/977-2 (1377-2)	174	178	194	193
AS-4/PEEK (APC-2)	150	137	167	157
IM8/HTA	262	253	273	264

*Temperature in °C, Heating Rate =10°C/min, Numbers in Parenthesis are Rescan

3.4 Mechanical Testing Results The results of the test matrix (Table 2) are given in Table 4. No measurements of error or standard deviation are given because of the low number of specimens tested.

3.4.1 0° Four-Point Flexure Results At room temperature all of the materials exposed to JP-4 had lower flex strength and moduli than the controls. The same trend was observed in the specimens tested at 82°C. With the exception of IM7/5250-4, the specimens tested at their respective elevated temperatures (See Table 2 for temperatures) exhibited no measurable difference in strength and modulus between the control specimens and those exposed to JP-4.

The decrease in room temperature properties could be attributed to several factors such as: a) decrease in matrix modulus due to plasticization, b) degradation of the fiber/matrix interface from the solvent absorption, or c) increased flaw sensitivity because of surface

Table 4. Mechanical Test Results

MATERIAL	CONDITION	0° 4-PT Flex*		90° 4-PT Flex**		0° 4-PT Shear*		+/-45° Tension**	
		RT	82 °C	RT	ETI***	RT	RT	RT	82 °C ETI***
AS-4 / 3501-6	CONTROL	MOD/STR (GPa/MPa)	MOD/STR (GPa/MPa)	MOD/STR (GPa/MPa)	MOD/STR (GPa/MPa)	STR (MPa)	MOD (GPa)	MOD (GPa)	MOD (GPa)
	JP-4	118.5/1841.0 86.0/1493.0	131.3/1698.0 87.9/1346.0	100.7/1161.0 101.3/1162.0	10.5/85.3 9.3/39.8	100.6 93.7	5.8 6.2	5.3 5.8	4.3 3.5
IM-7 / 5250-4	CONTROL	153.8/1772.0	170.8/1756.0	128.4/1131.0	10.4/83.4	100.4	7.0	6.8	5.9
	JP-4	111.1/1399.0	113.5/1330.0	113.3/1029.0	10.5/46.2	92.0	6.9	6.1	5.4
IM-7 / 8551-7A	CONTROL	151.3/1671.0	157.7/1468.0	138.9/1229.0	9.6/92.8	91.2	6.4	5.6	5.1
	JP-4	115.1/1259.0	105.3/1120.0	134.4/1216.0	9.3/47.9	74.6	6.5	5.4	5.4
IM-7 / 977-2	CONTROL	138.5/1678.0	147.9/1402.0	125.6/1048.0	10.2/107.6	96.8	5.7	5.7	4.5
	JP-4	107.1/1299.0	97.8/1116.0	122.4/1004.0	10.0/68.0	88.0	6.3	5.6	3.4
AS-4 / PEEK (APC-2)	CONTROL	141.0/1875.0	150.2/1619.0	125.7/1211.0	11.4/136.5	107.1	6.7	6.0	5.4
	JP-4	100.8/1515.0	102.7/1347.0	126.0/1234.0	11.2/135.8	99.2	5.9	5.4	2.3
IM-8 / APC (HTA)	CONTROL	169.9/1472.0	186.6/1277.0	152.8/865.0	8.8/99.2	85.0	4.9	4.8	4.0
	JP-4	122.3/1182.0	125.2/1084.0	153.0/949.0	9.0/82.6	89.5	4.7	4.1	3.4
*** ETI									
AS-4 / 3501-6	149 °C	* ASTM # D790-81							
IM-7 / 8551-7A	121 °C	length = 6.35 cm							
IM-7 / 5250-4	177 °C	width = 1.14 cm							
IM-7 / 977-2	149 °C	thickness = 0.16 cm							
AS-4 / PEEK (APC-2)	121 °C	** ASTM# D3518-76(82)							
IM-8 / APC (HTA)	177 °C	length = 13.9 cm							
		width = 1.91 cm							
		thickness = 0.10 cm							

crazing from the solvent absorption. With the exception of IM8/HTA the 0° laminates did not absorb an amount of fuel sufficient to plasticize the materials to the degree observed. In addition, crazing is usually observed in polymers exposed to very good solvents. JP-4 is not a good solvent for the matrix polymers evaluated. Degradation of the fiber/matrix interface could be a possible explanation for the observed decrease in four point flex properties. This phenomenon will be discussed further in the next section.

The elevated temperature results support the hypothesis that degradation of the interface could be occurring. There is no difference between the elevated temperature strength and modulus. In this temperature range the strength and moduli are insensitive to interfacial flaws.

3.4.2 90° Four-Point Flexure Results The [90°]_{12T} coupons were only tested at room temperature. There is no measurable difference in the moduli; however the strengths are dramatically lower in the coupons exposed to JP-4 than are the control coupons. The 90° flex is very sensitive to interfacial adhesion, thus this data supports the hypothesis that there is degradation of the fiber/matrix interface. The SEM photographs in Section 3.4.3 give some supporting evidence that the interface has degraded. The 90° flex is also very sensitive to surface flaws, such as crazing. However, SEM evaluation of the surfaces showed no evidence of crazing.

3.4.3 0° Four-Point Shear Results The 0° four point shear strengths of the coupons exposed to fuel were only slightly lower than the control coupons. More testing will be required to determine if the 0° four-point shear test is sensitive to the effects of fluid exposure on composites.

3.4.4 +/- 45° Tension Results The +/-45° tension test is used to determine the In Plane Shear (IPS) Modulus, G_{12} . G_{12} is very sensitive to the composite matrix, and is a good measure of plasticization due to solvent absorption. The angle-ply laminates also absorb much more solvent than do the unidirectional coupons. Thus, the IPS evaluation is viewed as a litmus test for fluid exposure testing.

Table 4 shows a measurable effect of the jet fuel exposure on G_{12} for most of the materials. The largest differences between the control specimens and those exposed to JP-4 were observed in the thermoplastics. The APC-2 was tested at an elevated temperature of 121°C which is above its fuel soaked Tg of approximately 106°C. Based on this we would expect

a dramatic drop in the modulus at 121°C. The APC-2 retains only 42% of the 121°C control G₁₂. The IM8/HTA also exhibits a significant drop in elevated temperature properties due to plasticization from the jet fuel. The IM8/HTA retains 84% of the 177°C control G₁₂.

3.5 Scanning Electron Microscopy Results Two example SEM photographs of 90° failure surfaces are shown in Figures 6 and 7. Figure 6 is the control IM7/8551-7A and Figure 7 is the IM7/8551-7A exposed to JP-4. The 90° flex strength of the fuel soaked specimen was only 52% of the control specimen; while the modulus of the fuel soaked specimen was 96% that of the control. Similar results were observed for all of the thermoset matrix composites evaluated. Our hypothesis is that the mixture of hydrocarbons must degrade the interfacial adhesion between the fiber and matrix. Visual evidence in the SEM photographs supports this belief. Broken out fibers in both photographs have matrix resin adhering to them. However, in Figure 7, several essentially clean fiber pull-out impressions are visible, while in Figure 6 no clean fiber impressions could be found. This indicates that there has been some degradation of the interface.

3.6 Desorption Results The jet fuel extracted from the APC-2 IPS sample was analyzed using GC-MS and the results are presented in Table 5. For purposes of comparison the GC-MS analysis of JP-4 used for exposure is also presented. The extracted fuel is nearly entirely composed of aliphatic substituted benzene components, while the JP-4 sample is predominately low molecular weight paraffin and olefin hydrocarbon components. To estimate some relative measure of concentration, all component peaks were normalized to the octane peak. Only one component, 1,2-dimethylbenzene, is common to both samples, but the desorbed sample has a concentration nearly 18X greater than in the JP-4 sample. Thus, it appears that the aromatic components of JP-4 are selectively absorbed and concentrated in the APC-2 specimen. A complete analysis of the GC-MS data is presented in a separate report (7).

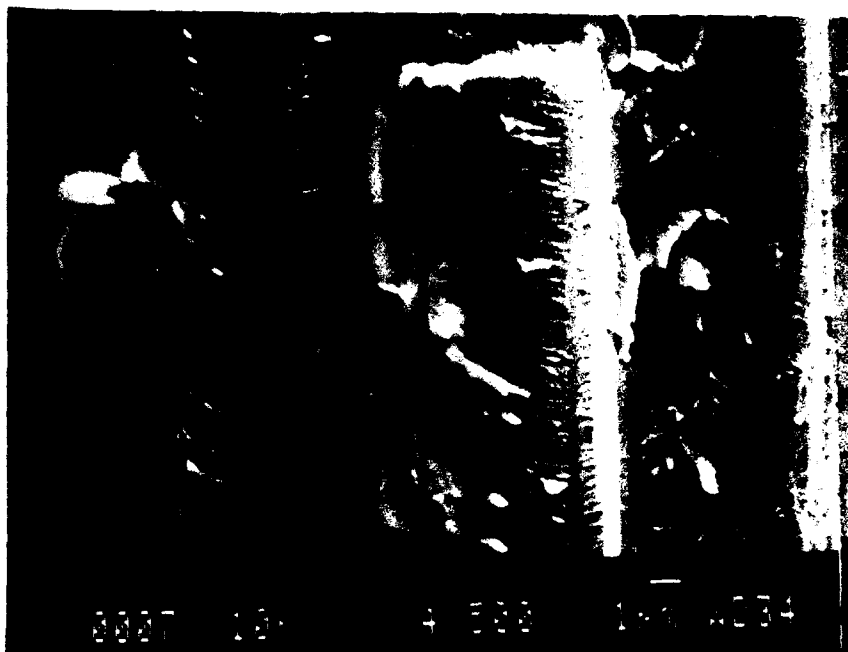


Figure 6. Scanning Electron Microscope photograph of the $[90^\circ]_{12T}$ flex failure surface of IM-7/8551-7A control specimen.



Figure 7. Scanning Electron Microscope photograph of the $[90^\circ]_{12T}$ flex failure surface of IM-7/8551-7A specimen exposed to JP-4.

Table 5. GC-MS Results (Octane is used as reference).

No.	Desorbed	A/Ao	JP-4	A/Ao
1	octane	1.0	2,3-dimethylpentane	2.3
2	1,2-dimethylbenzene	8.9	heptane	1.9
3	1-ethyl-3-methylbenzene	31.8	methylcyclohexane	1.4
4	1-ethyl-2-methylbenzene	9.4	octane	1.0
5	1,2,3-trimethylbenzene	34.4	2,6-dimethylheptane	0.1
6	1,2,4-trimethylbenzene	17.9	ethylcyclohexane	0.5
7	1-methyl-3-propylbenzene	8.8	2-methyloctane	0.4
8	1,4-diethylbenzene	32.2	1,2-dimethylbenzene	0.5
9	2-ethyl-1,4-dimethylbenzene	21.8	nonane	1.0
10	1,2,4,5-tetramethylbenzene	31.8	3,4,4-trimethyl-2-hexene	0.1

4. CONCLUSIONS

A technique was developed to expose composite materials to volatile and inflammable fluids at elevated temperatures. Exposure to JP-4 at elevated temperatures has been demonstrated to have a significant effect on the performance of advanced thermoplastic and thermoset matrix composite materials. The mechanism of property degradation on the thermoplastic matrix composites evaluated appears to be a plasticization of the matrix polymer. The mechanism in the thermoset matrix composites evaluated appears to be degradation of the fiber/matrix interface. Further work in this area will focus on the following topics: a) effect of the state of stress in the matrix on absorption of JP-4, b) investigation of the degradation of the fiber/matrix interface, c) use of high pressure dilatometry to measure the glass transition temperature of exposed specimens, and d) development of a model solvent to replace JP-4 for absorption studies.

5. REFERENCES

1. C.E. Browning, G.E. Husman, and J.M. Whitney in, Composite Materials: Testing and Design (Fourth Conference), ASTM STP 617, American Society for Testing and Materials, 1977, pp. 481-496.

2. C.D. Shirrell, and J. Halpin in, Composite Materials: Testing and Design (Fourth Conference), ASTM STP 617, American Society for Testing and Materials, 1977, pp. 481-496.
3. AF Contract No. F33615-86-C-5058 "High Temperature Thermoplastic Processing"
4. AF Contract No. F33615-84-C-5029 "Exploratory Development of Thermoplastic Composite Processing"
5. C.L. Hamermesh, Proceedings of the Sixth Industry/Government Review of Thermoplastic Composites (1989).
6. S.R. Lustig, Ph.D. Thesis, Purdue University, West Lafayette, IN (1989).
7. D.B. Curliss "The Effect of Jet Fuel on Advanced Aerospace Composites I: Thermal and Chemical Analysis," WRDC TR-90-XXXX, in preparation.